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Evaluation of phase II toxicity identification evaluation methods for freshwater whole sediment and interstitial water

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article info

abstract

Phase I whole sediment toxicity identification evaluation (TIE) methods have been developed to characterize the cause of toxicity as organic chemicals, metals, or ammonia. In Phase II identification treatments, resins added to whole sediment to reduce toxicity caused by metals and organics can be separated and eluted much like solid-phase extraction (SPE) columns are eluted for interstitial water. In this study, formulated reference sediments spiked with toxic concentrations of copper, fluoranthene, and nonylphenol were subjected to whole sediment and interstitial water TIE treatments to evaluate Phase I and II TIE procedures for identifying the cause of toxicity to Hyalella azteca. Phase I TIE treatments consisted of adding adsorbent resins to whole sediment, and using SPE columns to remove spiked chemicals from interstitial water. Phase II treatments consisted of eluting resins and SPE columns and the preparation and testing of eluates for toxicity and chemistry. Whole sediment resins and SPE columns significantly reduced toxicity, and the eluates from all treatments contained toxic concentrations of the spiked chemical except for interstitial water fluoranthene. Toxic unit analysis based on median lethal concentrations (LC50s) allowed for the comparison of chemical concentrations among treatments, and demonstrated that the bioavailability of some chemicals was reduced in some samples and treatments. The concentration of fluoranthene in the resin eluate closely approximated the original interstitial water concentration, but the resin eluate concentrations of copper and nonylphenol were much higher than the original interstitial water concentrations. Phase II whole sediment TIE treatments provided complementary lines of evidence to the interstitial water TIE results.

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1. Introduction

In an evaluation of waters throughout the United States, the USEPA found that 71% of 19,470 stations had sediment contamination that was either probably or possibly associated with harmful effects on aquatic life or human health (USEPA, 2004). Toxicity tests are among the primary tools used to assess sediment quality, and when tests indicate water quality impairment from toxic sediments, sites may be placed on the CWA §303[d] list of impaired waters (USEPA, 2004). States must then develop total maximum daily loads (TMDLs) for impaired waterbodies. A key component of the TMDL process is the identification of chemicals responsible for sediment toxicity (USEPA, 1998). This ensures that resources are directed at mitigating the actual causes of impairment (e.g., reducing the loads of the appropriate chemicals of concern).

One of the most important processes used to identify causes of sediment toxicity is the toxicity identification evaluation (TIE). TIEs involve a series of procedures designed to decrease, increase, or transform the bioavailable fractions of sediment contaminants to assess their contributions to sample toxicity (USEPA, 1991, 1993a,b). The three phases of the TIE process (characterization, identification, and confirmation) comprise a weight-of-evidence approach to determine the causes of toxicity. Phase I TIEs characterize the classes of chemicals causing toxicity and typically differentiate among ammonia, metals, or non-polar organic chemicals (Ho et al., 2004). Phase II TIE treatments identify the individual chemicals causing toxicity, and Phase III methods are designed to confirm the Phase II chemical identification. Additional lines of evidence are generated in sediment TIEs by manipulating both whole sediment and interstitial water samples. While TIE methods for freshwater and marine sediments have been under development for several years (Ankley et al., 1991; Besser et al., 1998; Kosian et al., 1999; Burgess et al., 2000, 2004, 2007; West et al., 2001; Ho et al., 2004; USEPA, 2007), most of the recent studies have focused on Phase I characterization treatments. Current efforts are focused on developing and evaluating whole sediment Phase II procedures for regulatory applications, such as TMDL development.

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The current study was part of a project designed to evaluate the effectiveness of existing sediment TIE procedures, and to assess whether these methods were sufficiently robust to identify specific chemicals responsible for toxicity. Results of the larger project are described in Anderson et al. (2007), but this study focuses on the evaluation of Phase II TIE methods for whole sediments and interstitial water. The goals of this paper are: (1) to demonstrate reduction of toxicity of spiked sediments with whole sediment amendments; (2) to evaluate the amendment elution process and demonstrate that toxic concentrations of chemicals from spiked sediments can be transferred to clean water as part of the identification phase of a TIE; (3) to evaluate the relationships between the concentrations of spiked chemical in the sediment, in the interstitial water, and in the TIE eluates; and (4) to compare the result of whole sediment and interstitial water TIE procedures.

2. Methods

2.1. Sediment spiking

Copper, fluoranthene and nonylphenol were spiked into clean reference sediment. These chemicals were chosen to represent chemical classes that are commonly encountered in highly polluted sediments. Reference sediment was created using equal parts sediment from a reference site in the Salinas River (Monterey County, California, USA), and clean, kiln-dried sand (#60, RMC Pacific Materials, Monterey, CA, USA). The sediment was amended with organic peat moss (Uni-Gro, Chino, CA, USA). One kilogram (dry weight) of formulated sediment was prepared by combining 496.25 g reference sediment, 496.25 g sand, and 7.50 g peat with 350 mL laboratory well water. The toxicity of the reference sediment was assessed with a standard 10 d H. azteca survival and growth toxicity test, and the sediment was analyzed for organochlorine, organophosphate and pyrethroid pesticides. The few contaminants detected were well below the tolerance threshold of the test organism. The average grain size of the formulated sediment was 61.18% sand and 38.82% fines, and the average total organic carbon (TOC) was 0.75%.

Methods used to spike copper into formulated sediment differed from those used to spike fluoranthene and nonylphenol. Copper chloride (Fisher Scientific, Fair Lawn, NJ, USA) stock solution was spiked directly into the water used to prepare the formulated sediment. This sediment was then rolled on a Wheaton roller apparatus (Wheaton Instruments, Millville, NJ, USA, Model 348940-48) for 24 h at 15 C. Fluoranthene (Supelco, Bellefonte, PA, USA) and nonylphenol (Sigma–Aldrich, St. Louis, MO, USA) chemical stock solutions were prepared in acetone and placed into 2000-mL glass jars where the solvent was allowed to volatilize under a fume hood (Ditsworth et al., 1990; Cole et al., 2000). After volatilization, formulated sediment was prepared in the containers and rolled for 24 h at 15 C. After initial rolling of spiked sediments, jars were transferred to a refrigerator for the remaining equilibration period at a temperature of 4 C. Copper was equilibrated for 14 d (Simpson et al., 2004); fluoranthene was equilibrated for 28 d (Cole et al., 2000), and nonylphenol was equilibrated for 7 d (Fay et al., 2000). Spiking concentrations were chosen based on the nominal median lethal concentrations (LC50 s) calculated from the results of range-finding tests (Anderson et al., 2007). After spiking and equilibration, a portion of the sediment was centrifuged to isolate interstitial water (30 min at 2500 g and 4 C.).

2.2. Toxicity Identification evaluations

Experiments focused on the removal of toxicity and the reduction of bioavailable contaminants with specific TIE treatments (Phase I), and the subsequent return of toxicity and chemicals to clean test media (Phase II). All methods are thoroughly described in Anderson et al. (2007). SIR-300 (ResinTech, West Berlin, NJ, USA), is a macroporous weak acid cation exchange resin which has chelating properties for metal ions, and is used to reduce bioavailability of cationic metals (Burgess et al., 2000), and was added to the copper-spiked sediment. Ambersorb 563 (Rohm and Haas, Spring House, PA, USA) is a carbonaceous resin used to reduce bioavailability of non-polar organic chemicals (Kosian et al., 1999), and was added to sediment containing fluoranthene and nonylphenol. Resins were thoroughly rinsed with Nanopure water, and one part resin was added to nine parts sediment (by wet weight) for a final concentration of 10%. At the termination of the whole sediment TIEs, the resins were isolated from the test sediment via sieving and subjected to Phase II TIE elution procedures. Portions of the recovered resins were rinsed with Nanopure water and eluted with hydrochloric acid (SIR-300) or acetone (Ambersorb) to recover sorbed metals and organics, respectively. An eluate treatment was created by adding the acid or solvent (evaporated to 1 mL) to 100 mL laboratory control water (well water). The volume of water for the eluate preparations was based on convenience and methodological consistency. The eluate was then tested using water-only exposures of amphipods and analyzed for the spiked chemical. In the results described below, discussion of the eluate chemistry refers to chemical concentrations in acid or solvent-spiked water used to assess toxicity.

The primary whole sediment Phase II TIE procedures used in this project were the recovery of resin amendments, the elution of amendments with solvents, and the analysis of eluates for toxicity and chemistry. Similarly, Phase II TIEs with interstitial water were conducted using two types of solid-phase extraction columns for organic and metal contaminants. The HLB column (Oasis Hydrophilic-Lipophilic Balance , 6 mL, 500 mg, Waters, Milford, MA, USA) is commonly used for the sorption of aqueous-phase non-polar organic compounds in analytical chemistry applications. The cation exchange column (Supelco Supelclean LC-WCX, 3 mL, St. Louis, MO, USA) was evaluated for interstitial water tests with copper. One hundred milliliters of interstitial water from spiked sediment was extracted by the respective columns in each procedure. Columns were eluted with acid or solvent, and the acid or solvent extracts were added to 100 mL laboratory control water for testing.

All whole sediment TIE treatments were conducted concurrently with treatment blanks consisting of un-spiked reference sediment which was subjected to the same TIE procedures. Dilution blanks were also included to account for any reduction in toxicity caused by dilution of contaminants with addition of amendments. Eluate treatments were accompanied by an acid or solvent control. All interstitial water TIEs were conducted using a dilution series of 0 (blank), 25, 50, and 100% sample. Laboratory control water was subjected to the TIE treatments and served as the treatment blank.

Hyalella azteca whole sediment exposures followed USEPA methods (USEPA, 2000), with the following modifications. Five replicate 250 mL beakers containing 50 mL sediment, 200 mL overlying water, and 10 amphipods were used for each whole sediment treatment. The exposures were conducted under static conditions for 10 d with slow aeration and were fed one mL YCT (yeast, cerophyll and trout chow) per beaker every other day. Interstitial water and eluate exposures were conducted in three replicate 20 mL scintillation vials containing 10 mL of water and five amphipods. Interstitial water tests were conducted for 10 d, and daily survival was recorded. All H. azteca were obtained from Chesapeake Cultures (Hayes, VA, USA) and were 7–14 d old at the time of test initiation.

Concentrations of spiked chemicals were measured in undiluted sediment, interstitial water, and eluate samples. Copper was measured in sediment using USEPA Method 200.8 (USEPA, 1994a,b) for water and USEPA Method 6020 (USEPA, 1990) for sediment. Fluoranthene was measured using USEPA Method 8270 (USEPA, 1994a,b). Nonylphenol was measured using California Department of Fish and Game Water Pollution Control Laboratory Method SUR01 (CDFG WPCL, Rancho Cordova, CA, USA).

2.3. Data analysis

The acceptability of each whole sediment or interstitial water TIE treatment blank was determined by comparing the survival to that of the negative control using a separate variance t-test (alpha = 0.05). The results of each individual TIE treatment were then compared to the baseline result (= untreated sample). The extraction efficiency of the whole sediment resin treatments was evaluated by determining the total mass of spiked chemical recovered in the solvent or acid extract of the resin, and dividing it by the total chemical mass in the whole sediment based on the measured sediment concentration. The calculated percentage recovery indicates the combined efficiency of chemical adsorption to the resin and solvent elution of the chemical from the resin.

Interstitial water treatments were evaluated using dilution series toxic units (DTUs) that were calculated by dividing 100 by the sample-specific LC50 calculated from the interstitial water dilution series. Comparing DTUs among the treatments provides better resolution than simply comparing single concentrations from the various dilution series. Chemical concentrations in the interstitial water and resin and column eluates were evaluated against published water-only LC50 concentrations for H. azteca. Chemical toxic units (CTUs) were calculated by dividing the measured chemical concentration by the published LC50 concentration for that chemical. The following LC50 concentrations were used: copper = 67.2 l g L^{-1} (Suedel et al., 1996), fluoranthene = 44 l g L^{-1} (Spehar et al., 1999), and nonylphenol = 21 l g L^{-1} (Brooke, 1993).

3. Results and discussion

All whole sediment test controls, treatment blanks, and elution blanks had >80% survival. The organism responses in the whole sediment dilution blanks were not significantly different from unamended spiked sediments, indicating that reductions of toxicity were not the result of sediment dilution. Survival levels in the blanks for column treatments of interstitial water in the copper and fluoranthene tests were significantly different from the negative control (26% and 40%, respectively). However, data from these treatments were still evaluated because survival in the remaining interstitial water dilutions from these treatments was not significantly different from the negative control.

All spiked sediments caused significant toxicity to H. azteca. Survival was 2, 8, and 0% for copper, fluoranthene and nonylphenol, respectively (Table 1). Addition of resin significantly increased survival in all spiked sediments. At test termination the resin was sieved from the sediment and eluted for the preparation of the eluate treatments. The mass of chemical recovered from the

resin ranged from 2% of the spiked mass of fluoranthene to 29% of the spiked mass of nonylphenol. These recoveries reflected the solubilities of the organic chemicals; more nonylphenol was recovered (log K_{ow} = 4.48) than fluoranthene (log K_{ow} = 5.12). In all cases the concentrations of spiked chemical in the resin eluates were greater than the LC50 concentrations for H. azteca and significant mortality was observed in the resin eluate treatments (Table 1).

In the whole sediment copper TIE, the concentration of total copper in the resin eluate greatly exceeded the LC50 concentration (50.2 mg L^{-1}, Table 1), but some survival (13%) was observed in the eluate treatment. We assume this reflects reduced copper bioavailability after resin treatment, but the reason for the observed survival is not clear. Reduced copper bioavailability could have occurred through the increase of the ionic concentration of the eluate during the neutralization process, specifically sodium and chloride (Di Toro et al., 2005). The specific conductivity of the eluate was 700 l S c m^{-1} prior to neutralization and 5800 l S c m^{-1} after neutralization. Conducting the eluate tests in small volume scintillation vials could have also contributed to reduced bioavailability through sorption of copper to the container walls. It was assumed, however, that the reduction of bioavailability was caused by the SIR-300 elution and neutralization process.

The SIR-300 method was originally developed by Burgess et al. (2000), and although they did not examine the bioavailability or toxicity of metals eluted from the resin, they measured total recovery of metals in the sediment, interstitial water, overlying water, and resin. In the treatment with resin, these authors measured a total recovery of 144%, compared to 115% in the treatment without resin. The high recovery in the resin treatments was attributed to interference from organic material associated with the resin that was released during metal analysis. In the current study it was assumed that some materials released from the resin interfered with the measured concentration of the eluted copper and reduced copper bioavailability.

Recovery of the spiked chemicals from the resins ranged from 2% to 29%, but these recovery values combine both adsorption to resin and elution from resin. Because chemical analysis was only conducted on the sediment, resin extract, and interstitial water, it was not possible to separate how much of the original chemical mass was sorbed to the resin versus how much of the sorbed mass was eluted. For example, the SIR-300 resin is capable of binding approximately 6 mg of copper per gram of resin. The copper-spiked sediment in the resin treatment contained approximately 170 mg of copper. Twenty-five grams of resin, with a binding capacity of 150 mg, was added to this treatment. An estimated 20 mg of copper was eluted from the resin, or 12% of the original mass. The capacity of the resin was sufficient to reduce copper toxicity, but the efficiency of the TIE elution process needs to be determined by eluting the resin several times and measuring the chemical concentrations in each solvent eluate.

These procedures are a first attempt to apply Phase II identification techniques in whole sediment TIEs, and show promise for identifying causes of sediment toxicity, but specific Phase II procedures require additional research. Ambersorb is no longer manufactured and Amberlite XAD-4 (Rohm and Haas, Spring House,

Table 1
Whole sediment and resin eluate chemistry and toxicity results.

Chemical	Concentration in sediment l g g^{-1}	Mean survival in sediment % (SD)	Mean survival in sediment with resin % (SD)	Percent of chemical recovered from resin %	Concentration in resin eluate mg L^{-1}	Hyalella water LC50 mg L^{-1}	Mean survival in resin eluate % (SD)
Copper	753	2 (4)	76 (11)	12	50.2	0.067	13 (12)
Fluoranthene	48.7	8 (18)	92 (8)	2	0.53	0.044	0 (0)
Nonylphenol	535	0 (0)	50 (29)	29	93	0.021	0 (0)

PA, USA) is considered a replacement. The performance of resins such as Amberlite or Tenax (Leppanen et al., 2003; You et al., 2007) should be evaluated to determine their efficacy in the TIE process (Anderson et al., 2007). We have conducted experiments with Amberlite and it exhibits the same toxicity reduction and elution characteristics as Ambersorb, but there are potential problems with the adsorption and elution of PAHs. It is possible that this resin will perform better with additional pre-treatment. Acetone was used to elute the Ambersorb in this study, but the performance of other solvents and elution procedures should be evaluated for different resins and chemicals. Lastly, the mixing and equilibration of the resin and sediment should be further evaluated to determine the optimal equilibration times and amendment addition ratios.

Conducting TIEs on interstitial water as well as whole sediment can provide additional lines of evidence to determine causes of toxicity. Significant toxicity was observed in the interstitial water isolated from spiked sediments (Table 2). Although the interstitial water baseline tests and TIE treatments were conducted using a dilution series, only the survival in undiluted interstitial water is presented in Table 2. Survival in the remaining dilutions was used to calculate DTUs, which indicate the reduction of toxicity in the interstitial water and are compared to CTUs (Table 3). Toxicity in all experiments was significantly reduced by passing the interstitial water through an SPE column. Although toxicity was reduced by the SPE columns, post-column concentrations of copper and nonylphenol were still greater than the LC50 concentrations for these chemicals due to incomplete removal by the column. Using columns with larger capacity would likely overcome the breakthrough of the chemicals. Toxic concentrations of copper and nonylphenol were eluted from the SPE columns and added to the eluate treatments. Only a small amount of fluoranthene was eluted from the column, and no toxicity was observed in the eluate treatment.

In several cases the measured concentration of chemical greatly exceeded the LC50 concentration, but survival was still observed in the treatment, suggesting that a large amount of the measured chemical was not bioavailable. In terms of CTUs, the interstitial water concentrations of copper and fluoranthene were equivalent to 212 and 10 CTUs, respectively, but some survival was observed in the lower concentrations of copper-spiked interstitial water and 50% survival was observed in undiluted fluoranthene-spiked interstitial water (Table 2). Similarly, survival was observed in the post-column interstitial water samples for copper and nonylphenol even though these samples contained 17 CTUs and 2 CTUs, respectively.

Dissolved organic carbon is one of the primary interstitial water components that can reduce chemical bioavailability (Suedel et al., 1993; Williamson and Burgess, 2000). There are two likely sources of DOC in the reference sediment interstitial water: carbon from the Salinas River reference site, or carbon from the peat that was added to create a final total organic carbon concentration of 0.75%. It is unlikely that a significant amount of DOC came from the peat because it is relatively insoluble (Eimers et al., 2002), therefore it is more likely that the DOC originated with the natural component of the reference sediment. Interstitial water DOC was not measured in these experiments, so we were not able to determine the role it played in chemical bioavailability. Other factors that might affect chemical bioavailability in interstitial water include sorption to test container surfaces and reduction through shifts in pH (Adams et al., 2000). Sorption to test container surfaces is a likely cause of reduced bioavailability because interstitial water tests and resin elution tests were conducted in 20 mL vials containing 10 mL of sample. There was therefore a large surface-to-volume ratio in the interstitial water and eluate tests.

The measured chemical concentrations in the interstitial water, post-column sample, resin eluate, and column eluate were converted to CTUs based on published water-only LC50 concentrations (Table 3). The CTUs were used to evaluate relative chemical concentrations among the various treatments in terms of their toxicity, and to compare measured chemical concentrations to observed toxicity using DTUs. The CTUs in the post-column samples ranged from 0.8% to 8% of the interstitial water CTUs, demonstrating that the columns removed over 90% of the chemicals. During the column elution process over 100% of the nonylphenol was recovered, whereas approximately 55% of copper and less than one percent of fluoranthene was recovered. Fluoranthene had the most complete removal by the column, but the lowest recovery. The manufacturer's generic instructions for loading and eluting the column were followed in the interstitial water TIEs. These methods were apparently adequate for nonylphenol, but in this study and a related study (Anderson et al., 2007), elution of fluoranthene from the HLB column was poor. The relationships between the chemical concentrations in the interstitial water, HLB column eluate and whole sediment resin eluates were inconsistent. The concentrations in the copper and nonylphenol whole sediment resin eluates greatly overestimated the interstitial water concentration, yet the resin eluate concentration of fluoranthene closely approximated that of the interstitial water. This result was in contrast to the interstitial water experiments in which the

Table 2
Undiluted interstitial water and column eluate chemistry and toxicity results.

	Concentration in interstitial water mg L^{-1}	Mean survival in interstitial water % (SD)	Mean survival in post-column sample % (SD)	Concentration in post-column sample mg L^{-1}	Concentration in column eluate mg L^{-1}	Hyalella water LC50 mg L^{-1}	Mean survival in column eluate % (SD)
Copper	14.2	0 (0)	73 (12)	1.11	7.83	0.067	0 (0)
Fluoranthene	0.451	50 (10)	93 (12)	0.0037	0.0027	0.044	100 (0)
Nonylphenol	1.03	0 (0)	58 (23)	0.045	1.04	0.021	0 (0)

Table 3
Chemical concentrations expressed as CTUs and magnitude of toxicity expressed as DTUs in interstitial water, post-column sample, column eluate, and resin eluate. Chemical toxic units are calculated by dividing the measured concentration by the median lethal concentration (LC50) for that chemical. Dilution series toxic units are calculated by dividing 100 by the percentage LC50 calculated from the dilution series.

	Interstitial water		Post-column sample		Column eluate		Resin eluate
	CTU	DTU	CTU	DTU	CTU	DTU	CTU
Copper	212	7.4	17	<1	117	P8	749
Fluoranthene	10	1	0.08	<1	0.06	<1	12
Nonylphenol	49	P8	2	<1	50	P8	4429

nonylphenol column eluate most closely approximated the interstitial water concentration.

The high concentrations of copper and nonylphenol in the resin eluates were most likely the result of the resin driving the equilibrium in the sediment during the exposure. In experiments with Tenax, another highly adsorbent resin, it was determined that the rapidly desorbing and currently bioavailable fraction of the chemicals in the test sediment adsorbed to the resin in less than 30 h (Cornelissen et al., 2001). However, the application of TIE resins is to reduce the bioavailable fraction for the duration of the exposure as the exposure system continues to equilibrate. In the case of some chemicals, it is inevitable that large concentrations of chemical are recovered from the resin and are transferred to the eluate treatments. Perhaps because of it s lower solubility a lesser amount of fluoranthene sorbed to the Ambersorb during the toxicity exposure. The variability of the sorption process, resulting in variable resin eluate concentrations, causes the Phase II whole sediment treatment to provide more qualitative results. This does not lessen its importance as a complementary Phase II treatment to the interstitial water SPE columns and eluates.

Dilution series toxic units are often used to interpret interstitial water TIE data because they provide resolution among the different sample concentrations, and therefore may be used to compare the change in toxicity among treatments. It is assumed that if an interstitial water sample contains a single toxicant, the calculated DTUs for that sample should be equivalent to the CTUs of the chemical in the sample. For example, if a sample contains 2 CTUs of copper, then the LC50 calculated from the dilution series should be 50% sample, or 2 DTUs. However, one factor affecting the accuracy of toxic units based on the dilution series are the number of dilutions tested. If the lowest concentration of interstitial water tested is 25%, and complete mortality is observed in all concentrations including 25% interstitial water, then the sample contains greater than or equal to 8 DTUs. The toxic units for nonylphenol in interstitial water, and copper and nonylphenol in the column eluate might have been more comparable if additional dilutions had been tested (Table 3). Interstitial water toxic units for copper and fluoranthene, and post-column sample toxic units for copper and nonylphenol were not comparable because of lower than expected toxicity due to reduced bioavailability, as discussed above. The fluoranthene toxic units in the post-column sample and the column eluate were comparable. Although toxic units in general can be a valuable tool for interpreting TIE data, the results of this study demonstrate that the relationship between CTUs and DTUs should be evaluated with caution. Because of factors affecting chemical bioavailability, CTUs may over or underestimate toxicity and calculation of interstitial water DTUs is affected by the number of dilutions used in the toxicity test for each treatment. CTUs based on published LC50s can be variable because they were generated in waters with varying chemistry. If published LC50s are used to identify the cause of toxicity in a Phase II TIE, these concentrations should be verified as part of the confirmation process in a Phase III TIE.

The Phase II TIE procedures evaluated in this study were performed on reference sediments spiked with a single known contaminant. Based on previous studies (Kosian et al., 1999; Burgess et al., 2000) the whole sediment treatments were expected to reduce toxicity, and in the case of the interstitial water column extractions, identify toxicity (USEPA, 1993a,b). The whole sediment Phase II procedures investigated here have not been widely studied, but were conducted concurrently with the interstitial water procedures to assess whether they provided additional lines of evidence in support of the interstitial water results. In all cases, the resin amendments reduced whole sediment toxicity in situations where the SPE columns reduced interstitial water toxicity. All of the whole sediment eluates contained toxic concentrations of the spiked chemicals, whereas fluoranthene did not elute from the SPE column in interstitial water tests. Total concentrations of the chemicals in some interstitial waters, post-column samples, and the copper resin eluate exceeded published LC50 concentrations, but survival was still observed, indicating some portion of the measured chemical was not bioavailable. Reduced bioavailability, whether caused by the interstitial water or a product of the TIE treatment, should be taken into consideration when interpreting Phase II TIE data.

For TIEs to be effective tools in developing appropriate sediment TMDLs the TIE methods must have a sufficient degree of specificity to identify the chemicals responsible for toxicity. Based on results of this study, whole sediment and interstitial water Phase I TIE procedures were able to characterize the cause of toxicity from a single spiked chemical, and Phase II elution procedures provided additional lines of evidence to identify the cause of toxicity. The Phase II TIE methods for both whole sediment and interstitial water applications need additional development and fine tuning, and should be considered guidance (USEPA, 2007), but this study demonstrates the continuing advancement of sediment TIE methodology.

Acknowledgement

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